

4 Entropy

4.1 The Second Law of thermodynamics

4.1.1 Formulation and exploitation

- *Formulation*

Rudolf Julius CLAUSIUS (1822-1888) has drawn conclusions from the following experience

Heat cannot pass by itself from a colder to a warmer body

or, in a later version

Heat cannot pass from a colder to a warmer body without compensation.

These are two formulations of the Second Law of thermodynamics.

We have already mentioned – as an assumption – that there are always positive and negative parts of the heat exchanged with a heat engine. Indeed, this is a consequence of the Second law. If it were different, we should be able to convert the heat of a part of the cold sea fully into work, and then convert the work back into heat by stirring a hot liquid. In this manner, in effect, heat would have passed from the cold sea to the hot liquid and this contradicts the Second Law. William THOMSON (Lord KELVIN) has used this argument to express the Second Law in an alternative form, *viz.*

It is impossible to gain work in a heat engine by just cooling a body.

All of these statements are open to the criticism that they are verbally expressed and lack the stringency of mathematical formulae. It is a somewhat idle effort, however, to try and make these suggestive formulations strict, because in the end, when we have gone through CLAUSIUS's argument, there is a mathematical formula, an inequality, and this is the proper mathematical form of the Second Law – and that *is* strict.

- *Universal efficiency of the Carnot process*

CLAUSIUS exploits his Second Law by attempting to contradict it with the operation of two Carnot engines I and II of which one is a heat engine, while the other one is a heat pump or a refrigerator. The engines may employ different working agents in different ranges of density, but they do operate between the same temperatures, denoted by T_L and $T_H > T_L$. The work produced by one engine is consumed by the other one. The heat engine absorbs the heat Q_H at the temperature T_H and gives off the heat $|Q_L|$ at T_L . If it were different, we should have a transition from cold to hot and work produced, and that contradicts the Second Law.

In a first step – always following CLAUSIUS – we consider reversible Carnot engines, *cf.* Fig. 4.1. The arrows represent the direction of the cyclic processes. The strategy of the argument is to let both engines run through an equal number of

cycles, so that no work is left over, and then compare the heats exchanged at T_L and T_H . By (3.13) we have

$$-W_o^I = Q_L^I - |Q_H^I| < 0 \quad \text{and} \quad -W_o^{II} = Q_H^{II} - |Q_L^{II}| > 0. \quad (4.1)$$

Hence follows from $-W_o^I = W_o^{II}$

$$Q_L^I - |Q_H^I| = -(Q_H^{II} - |Q_L^{II}|) \Rightarrow Q_L^I - |Q_L^{II}| = |Q_H^I| - Q_H^{II}. \quad (4.2)$$

Now let us assume that $Q_L^I - |Q_L^{II}| > 0$ holds so that engine I absorbs more heat at T_L than engine II delivers there. In this case (4.2) implies that engine I delivers more heat at T_H than engine II absorbs there. In effect – after both engines have run through equally many cycles – the result is a transition of heat from T_L to T_H and that is forbidden. But the alternative $Q_L^I - |Q_L^{II}| < 0$ is also forbidden. To be sure: If engine I absorbs less heat at T_L than engine II delivers there, the two engines would effect a transition of heat from high to low temperature which is allowed. However, the engines are reversible and when we reverse their operation, the heats are reversed and we are brought back to the former impossible situation.

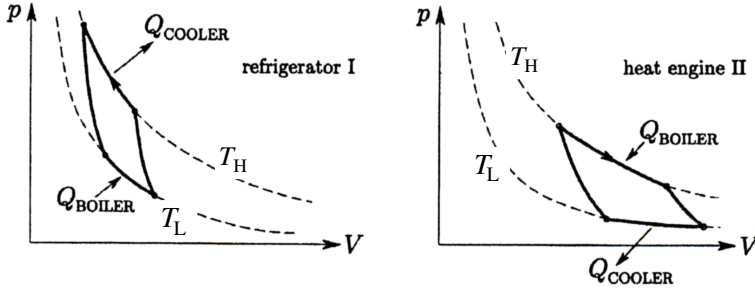


Fig. 4.1 CLAUDIUS's competing Carnot engines.

Therefore the only possible case is

$$Q_L^I = |Q_L^{II}| \quad \text{and, by (4.2)} \quad |Q_H^I| = Q_H^{II}. \quad (4.3)$$

It follows that the efficiencies of both engines are equal, because we have

$$e_C^I = \frac{W_o^I}{|Q_H^I|} \quad \text{and} \quad e_C^{II} = \frac{-W_o^{II}}{Q_H^{II}} \quad \text{or, by (4.3)} \quad e_C^I = e_C^{II}. \quad (4.4)$$

Since both engines may be working with different agents, (4.4) implies that the efficiency of a Carnot engine is universal, *i.e.* independent of the agent, be it a gas, a vapor, a liquid, or a solid. Since this is so, we may identify the efficiency with the one of an ideal gas. Therefore (3.17) holds for all agents and we write

$$e_C = 1 - \frac{T_L}{T_H}. \quad (4.5)$$

• *Absolute temperature as an integrating factor*

By (4.4) and (4.5) we conclude for the reversible Carnot process of a heat engine

$$e_C = \frac{-W_o}{Q_H} = \frac{Q_H - |Q_L|}{Q_H} = 1 - \frac{|Q_L|}{Q_H} = 1 - \frac{T_L}{T_H}.$$

The last equation implies

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0. \quad (4.6)$$

Thus the quantity Q/T enters the heat engine at high temperature and leaves it – unchanged in value – at low temperature. CLAUSIUS calls this quantity the *entropy* and denotes it by S . We may write $S_H = S_L$ and conclude that the entropy passes through the engine from hot to cold, unchanged in amount. It follows that at the low temperature the heat delivered is smaller than the heat absorbed at the high temperature. The heat difference is, of course, the work.

Up to this point CLAUSIUS's reasoning concerned Carnot cycles and their efficiency. But now starts a chain of arguments which extrapolates the equation (4.6) so that in the end we shall arrive at an equation for an arbitrary cycle. Hence follows the generalization of the concept of entropy and some properties of this quantity. We develop the argument in two steps.

The statement (4.6) may easily be generalized to reversible cycles that consist of isotherms and adiabates, cf. Fig. 4.2 a. and the octagone emphasized there by bold lines. The two dashed lines show how the process may be decomposed into three Carnot cycles a , b , and c . For each one we have the equivalent of (4.6), viz.

$$\frac{Q_H^a}{T_H^a} + \frac{Q_L^a}{T_L^a} = 0, \quad \frac{Q_H^b}{T_H^b} + \frac{Q_L^b}{T_L^b} = 0, \quad \frac{Q_H^c}{T_H^c} + \frac{Q_L^c}{T_L^c} = 0. \quad (4.7)$$

From Fig. 4.2 a. we identify

$$T_H^a = T_H^b = T_1, \quad T_H^c = T_2, \quad T_L^b = T_L^c = T_4, \quad T_L^a = T_3.$$

Therefore the sum of the three equations (4.7) gives

$$\frac{Q_H^a + Q_H^b}{T_1} + \frac{Q_H^c}{T_2} + \frac{Q_L^a}{T_3} + \frac{Q_L^c + Q_L^b}{T_4} = 0,$$

or with Q_i for the heat exchanged at temperature T_i

$$\sum_{i=1}^4 \frac{Q_i}{T_i} = 0. \quad (4.8)$$

The process curve of any reversible cycle may be approximated by a zig-zag line of isotherms and adiabates in the manner indicated in Fig. 4.2 b. When this zig-zag line is constructed, one must take care that the heat exchanged on each of the infinitesimal isothermal branches is equal to the heat exchange on the smooth curve; the blow-up in Fig. 4.2 b. shows how this can be achieved: The shaded areas in each step must be equal. By this construction we also ensure that the work of the smooth cycle is equal to that of the zig-zag curve, since the areas inside the

curves are equal. As far as heat and work are concerned, the process is thus equivalent to a combined process of many infinitesimal Carnot cycles.

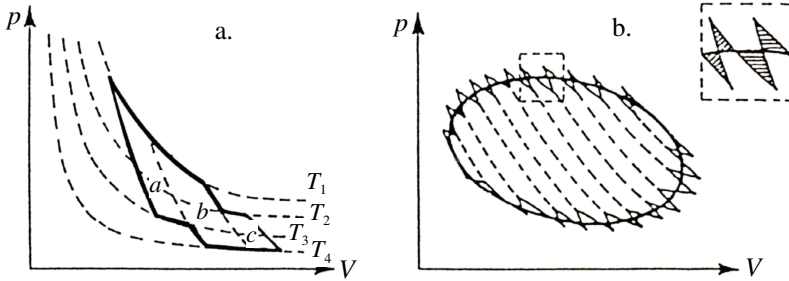


Fig. 4.2 a. A reversible cycle of isotherms and adiabates

b. An arbitrary reversible cycle decomposed into isotherms and adiabates.

Given this we may now apply the argument, which has led to (4.8), to the complex cycle of Fig. 4.2 b. The heat exchanged on an infinitesimal isothermal step is $\dot{Q}dt$, and the entropy exchange is

$$dS = \frac{\dot{Q}dt}{T}. \quad (4.9)$$

Integration over the cycle between the initial and final times gives

$$\int_{t_i}^{t_f} \frac{\dot{Q}dt}{T} = 0, \quad (4.10)$$

since the entropy exchange dS – or $\frac{\dot{Q}dt}{T}$ – goes in and out of the infinitesimal Carnot cycles unchanged in amount. By (3.4) the equation (4.9) may be written in the form

$$dS = \frac{1}{T}(dU + pdV). \quad (4.11)$$

Obviously the entropy S is a function of U and V , and we may express (4.11) by saying that the absolute temperature is an integrating denominator of the differential form $(dU + pdV)$.

- *Growth of entropy*

We continue to pursue CLAUSIUS's argument on the competition of Carnot engines that work between the temperatures T_L and T_H and of which engine II is a heat engine whose work drives the heat pump or refrigerator I. Now, however, we assume that engine II does not work *reversibly*, such that the heats exchanged at T_L and T_H are not reversed when the operation of the engine is reversed.

The relation (4.2) continues to hold and we assume that engine I absorbs more heat at temperature T_L than engine II delivers there. The net result is that heat has

moved from cold to hot and this is forbidden by the second law. We consider the alternative: Engine I absorbs less heat at T_L than engine II delivers there. In this situation heat passes from hot to cold, which is allowed. Nor can this possibility be excluded – as it was previously – by reversing the direction of operation of the engines. After all, engine II is not reversible.

Therefore we conclude from (4.2) that we must have

$$Q_L^I - |Q_L^II| = |Q_H^I| - Q_H^II < 0,$$

i.e. the absorbed heat Q_H^I of the reversible *heat engine* I is smaller than the absorbed heat Q_H^II of the irreversible heat engine II, or else we have

$$\frac{-W_o^I}{Q_H^I} > \frac{-W_o^II}{Q_H^II} \quad \text{or} \quad e_C^I > e_C^II. \quad (4.12)$$

Thus the efficiency of the reversible engine is greater than the efficiency of the irreversible one. But, since engine I is reversible, we have $e_C^I = 1 - T_L/T_H$ and therefore by (4.12)₁ and with $-W_o^II = Q_H^II - |Q_L^II|$

$$e_C^I = 1 - \frac{T_L}{T_H} > 1 + \frac{Q_L^II}{Q_H^II} \quad \text{or} \quad \frac{Q_H^II}{T_H} + \frac{Q_L^II}{T_L} < 0. \quad (4.13)$$

The inequality (4.13) now replaces the equation (4.6). The latter one led to (4.10) in a sequence of steps which we may repeat for the present case. Thus we arrive at the inequality

$$\int_{t_i}^{t_f} \frac{\dot{Q} dt}{T} < 0 \quad (4.14)$$

which must hold for an arbitrary irreversible cycle.

In order to proceed further we decompose the irreversible cycle between the times t_i and t_f into an irreversible branch between t_i and t_m and a reversible branch between t_m and t_f . We obtain

$$\int_{t_i}^{t_m} \frac{\dot{Q} dt}{T} + \int_{t_m}^{t_f} \frac{\dot{Q} dt}{T} < 0. \quad (4.15)$$

By (4.9) the second integral may be evaluated; it turns out to be equal to $S_f - S_m$ or $S_i - S_m$, since $S_f = S_i$. Hence we obtain from (4.15)

$$S_m - S_i > \int_{t_i}^{t_m} \frac{\dot{Q} dt}{T} \quad (4.16)$$

In words: The entropy change in an irreversible process is greater than the accumulated heating, divided by the temperature at which the heating occurs.

- (T, S) -diagram and maximal efficiency of the Carnot process

When the thermal and caloric equation of state are given, the equation (4.11) may be used to calculate $S = S(T, V)$ by integration to within an additive constant. After that has been done, a reversible cycle of a heat engine may be represented by a closed curve in a (T, S) -diagram, cf. Fig. 4.3 a. Such a diagram has several advantages:

- From (4.9) it follows that $Q_+ = \int T dS$ holds when the integration is carried out over the upper part of the curve. Therefore the area below the upper part of the curve is equal to Q_+ .
- Likewise $Q_- = \int T dS$ holds by integration over the lower part of the curve. Therefore the area below the cycle is equal to $|Q_-|$.
- Furthermore we have $-W_o = Q_+ - |Q_-|$ so that $|W_o|$ is equal to the area inside the curve. This property is shared by the (T, S) -diagram and by the (p, V) -diagram, cf. Section 3.1.
- A reversible adiabatic process is an *isentropic* process, because we have $dS = \dot{Q} dt = 0$. This means that the process is represented by a vertical line in the (T, S) -diagram.

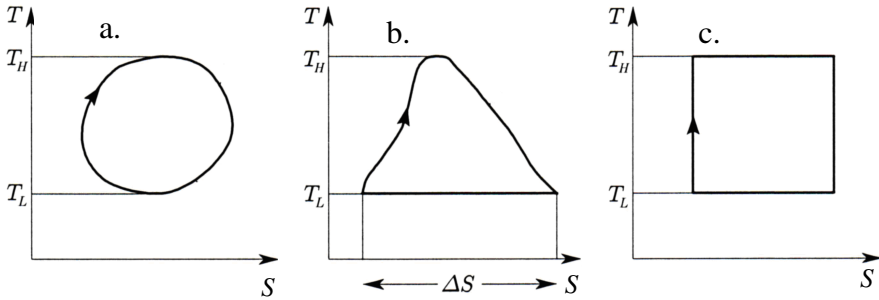


Fig. 4.3 a. Reversible cycle in the (T, S) -diagram

b. Cycle with cooling at T_L

c. Carnot cycle.

By use of the (T, S) -diagram we may find out – purely geometrically – which reversible cycle, running between an upper temperature T_H and a lower one T_L , has the largest efficiency. Fig. 4.3 shows three cycles of that type, all with the same value Q_+ , the area below the upper part of the process curve. We may increase the efficiency

$$e = 1 - \frac{|Q_-|}{Q_+}$$

at constant Q_+ by making $|Q_-|$, the integral $\int T dS$ along the lower part of the curve, as small as possible. This is achieved by releasing all heat at the lowest temperature T_L , see Fig. 4.3 b. In this case $|Q_-| = T_L \Delta S$ and $|Q_-|$ becomes minimal, when ΔS is made as small as possible. Now, a smaller ΔS – for fixed Q_+ – is realized when the temperature of the added heat is increased. And ΔS becomes minimal, when all contributions to Q_+ are added at the highest temperature T_H . Thus in the (T, S) -diagram a rectangle appears, defined by two horizontal isotherms and two vertical isentropes. This process curve is the one of the Carnot process.

The argument confirms what has merely been stated before, namely that the Carnot process has the largest efficiency among reversible cycles between the temperatures T_H and T_L . To be sure there are other cycles with the same efficiency, e.g. the Erickson cycles and the Stirling cycle in ideal gases, – cf. Paragraph 3.4.2 – but those require regeneration. Also their efficiency is not universal.

4.1.2 Summary

For reversible processes in closed systems for which, by (1.57), the First Law reads

$$\dot{Q} dt = dU + p dV, \quad (4.17)$$

the Second Law implies that $\dot{Q} dt$, the exchanged heat, changes a quantity S , the entropy which depends on the states (U, V) , or (T, V) , or (p, V) , etc. The change of entropy amounts to $\dot{Q} dt$ divided by the absolute temperature, so that we have

$$dS = \frac{\dot{Q} dt}{T} \quad \text{or by (4.17)} \quad (4.18)$$

$$dS = \frac{1}{T} (dU + p dV) \quad \text{or with } U = U(T, V) \quad (4.19)$$

$$dS = \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V dT + \frac{1}{T} \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] dV. \quad (4.20)$$

The equations (4.19) or (4.20) are known as *Gibbs equation*. In words the equation may be expressed by saying that the absolute temperature serves as an *integrating denominator* of the expression $dU + p dV$.

For irreversible processes the Second Law implies that the change of entropy between the initial time t_i and the final time t_f satisfies the inequality

$$S_f - S_i > \int_{t_i}^{t_f} \frac{\dot{Q} dt}{T}. \quad (4.21)$$

The relations (4.18) and (4.21) may be summarized by the *Clausius inequality* in the form

$$S_f - S_i \geq \int_{t_i}^{t_f} \frac{\dot{Q} dt}{T}, \text{ or for short processes } \frac{dS}{dt} \geq \frac{\dot{Q}}{T}, \quad (4.22)$$

where the equality holds for irreversible processes.

In particular (4.22) implies that the entropy cannot decrease in an adiabatic process; in equilibrium, at the end of the process, the entropy is maximal.

Of course, the usefulness of the Second Law must not exhaust itself in the introduction and characterization of a quantity, the entropy, which we have not missed up to now. The knowledge to be gained from entropy, Gibbs equation, and Clausius inequality will be discussed in Sect. 4.2 and in later chapters.

One point which we may now understand concerns the occurrence of $|Q_-| \neq 0$ in every cycle. Indeed a cycle has always parts with Q_+ and Q_- . This is made obvious by Fig. 4.3 and the discussion of the (T, S) -diagram. It is therefore impossible to run a working cycle by only absorbing heat from a reservoir without releasing heat during certain parts of the cycle. This is the statement which Kelvin chose as his version of the Second Law, see Paragraph 4.1.1.

The Gibbs equation (4.19) makes a statement about the function $S(U, V)$. Equally well we may write it – for a fluid in a *reversible process* characterized by $U(t)$ and $V(t)$ – in the form

$$\frac{dS}{dt} = \frac{1}{T} \left(\frac{dU}{dt} + p \frac{dV}{dt} \right).$$

This gives the rate of change of S in time when U and V , hence $p=p(U, V)$ and $T=T(U, V)$, change in time.

On the other hand in an *irreversible process* we have the Clausius inequality (4.22) or, by (1.53)₁

$$\begin{aligned} \frac{dS}{dt} &> \frac{1}{T} \left(\frac{d(U + K)}{dt} - \dot{W} \right) \text{ or, by (1.53)}_2 \\ \frac{dS}{dt} &> \frac{1}{T} \left(\frac{d(U + E_{\text{pot}} + K)}{dt} - \dot{W}_{\text{stress}} \right) \end{aligned}$$

There is no Gibbs equation in this case;* the inequality provides a lower bound on the rate of change of entropy in terms of the fields $\rho(x_j, t)$, $w_i(x_j, t)$, and $T(x_j, t)$ inside the system, and of the working of the stress on the boundary.

Note also that T in the Clausius inequality is always the homogeneous temperature on the boundary, or at least on that part of the boundary across which heat is exchanged. In a reversible process this boundary temperature is equal to the homogeneous temperature throughout the system, but not in an irreversible process,

* Except perhaps locally, cf. Chap. 12

where generally we have arbitrary fields inside the system, including an arbitrary temperature field.

4.2 Exploitation of the Second Law

4.2.1 Integrability condition

We start with the Gibbs equation in the form (4.20). Mathematicians call an expression like that a total differential. The relation is a short form of expressing two differential equations, namely

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{1}{T} \left(\frac{\partial u}{\partial T}\right)_v \quad \text{and} \quad \left(\frac{\partial s}{\partial v}\right)_T = \frac{1}{T} \left[\left(\frac{\partial u}{\partial v}\right)_T + p \right], \quad (4.23)$$

where we have switched to specific values by dividing (4.20) by the mass of the body.

Mixed second derivatives can be interchanged. Therefore we must have

$$\left(\frac{\partial}{\partial v} \left[\frac{1}{T} \left(\frac{\partial u}{\partial T} \right)_v \right] \right)_T = \left(\frac{\partial}{\partial T} \left[\frac{1}{T} \left[\left(\frac{\partial u}{\partial v} \right)_T + p \right] \right] \right)_v.$$

The mixed second derivatives of u cancel and a short calculation will then show that

$$\left(\frac{\partial u}{\partial v} \right)_T = -p + T \left(\frac{\partial p}{\partial T} \right)_v. \quad (4.24)$$

The significance of this equation can hardly be overestimated. It saves infinitely much money and labor, because it relates the caloric equation of state to the thermal equation of state. Let us consider this:

We recall that the thermal equation of state is relatively easy to determine, while the determination of the caloric equation of state requires many measurements of c_p and c_v , the specific heats. And those, being caloric measurements, are difficult, expensive, and unreliable. The integrability condition (4.24) helps us to reduce the number of caloric measurements *drastically* and therein lies its importance.

Indeed, in Paragraph 2.3.3 we have seen that the determination of $\left(\frac{\partial u}{\partial T}\right)_v$ and $\left(\frac{\partial u}{\partial v}\right)_T$ makes it necessary to measure c_p and c_v for all pairs of (v, T) . Now, since by the integrability condition (4.24) the derivative $\left(\frac{\partial u}{\partial v}\right)_T$ may be calculated from the thermal equation of state, *we do not need to measure c_p anymore*. And this is not all yet: If we differentiate (4.24), left and right, with respect to T , we obtain

$$\frac{\partial^2 u}{\partial T \partial v} = T \left(\frac{\partial^2 p}{\partial T^2} \right)_v \quad \text{or, with} \quad c_v = \left(\frac{\partial u}{\partial T} \right)_v : \quad \left(\frac{\partial c_v}{\partial v} \right)_T = T \left(\frac{\partial^2 p}{\partial T^2} \right)_v. \quad (4.25)$$

It follows that the v -dependence of c_v follows from the thermal equation of state as well. All that remains to be measured is c_v for *one* choice of v as a

function of T . Thus the number of required caloric measurements has indeed been reduced most severely.

4.2.2 Internal energy and entropy of a van der Waals gas and of an ideal gas

An example for the partial determination of the caloric equation $u(v, T)$ from the thermal equation $p(v, T)$ is furnished by the van der Waals gas, cf. Paragraph 2.4.9. Here we know only the thermal equation of state (2.33). However, the integrability condition (4.24) allows us to determine the v -dependence of $u(v, T)$, viz.

$$\left(\frac{\partial u}{\partial v}\right)_T = +\frac{a}{v^2}, \text{ hence } u(v, T) = -\frac{a}{v} + F(T), \quad (4.26)$$

where $F(T)$ is a constant of integration, namely a constant with respect to v .

Furthermore, by (4.25), c_v is independent of v in a van der Waals gas, because p is a linear function of T . The constant of integration $F(T)$ may therefore be written as $\int c_v(T) dT$, because, by (4.26), we have $c_v = F'(T)$. Therefore the generic form of the caloric equation of state for a van der Waals gas reads

$$u(v, T) = -\frac{a}{v} + \int c_v(T) dT. \quad (4.27)$$

In order to determine it fully we must measure $c_v(T)$. Note that the van der Waals case is a little too simple to be typical, because in general c_v will not only depend on T but also on v .

By use of the Gibbs equation (4.20) we may now calculate the specific entropy of a van der Waals gas. By (4.20), (4.24), and (4.27) we obtain

$$ds = \frac{1}{T} c_v(T) dT + \left(\frac{\partial p}{\partial T}\right)_v dv \text{ or, by (2.33)}$$

$$ds = \frac{1}{T} c_v(T) dT + \frac{\frac{R}{M}}{v-b} dv \text{ or, by integration} \quad (4.28)$$

$$s = \int \frac{c_v(T)}{T} dT + \frac{R}{M} \ln(v-b). \quad (4.29)$$

The integral term, of course, contains an arbitrary constant.

The entropy of an ideal gas follows from (4.29) as the special case, where c_v is constant and b is zero. We have

$$s(v, T) = c_v \ln T + \frac{R}{M} \ln v + \beta', \quad (4.30)$$

where β' is a constant of integration. Often s is expressed as a function of T and p , rather than T and v . Since $p v = \frac{R}{M} T$ and $c_p - c_v = \frac{R}{M}$ hold, we obtain

$$s(T, p) = c_p \ln T - \frac{R}{M} \ln p + \beta, \quad (4.31)$$

where $\beta = \beta' - \frac{R}{M} \ln \frac{R}{M}$.

The value of the additive constants in energy and entropy are of no interest until we come to consider chemical reactions, *cf.* Chap. 8. For all other processes they drop out of the relevant equations.

We know now that a reversible adiabatic process is isentropic so that $s = \text{const}$ holds in such a process. Thus (4.30) with $c_p - c_v = \frac{R}{M}$ and $\kappa = \frac{c_p}{c_v}$ implies

$\frac{p^{\frac{\kappa-1}{\kappa}}}{T} = \text{const}$, a relation which we have previously called an “adiabatic equation of state”, *cf.* (1.62). Of course, this only means that our concepts and calculations are consistent, at least with respect to isentropy.

4.2.3 Alternatives of the Gibbs equation and its integrability conditions

By easy manipulations the Gibbs equation (4.19) may be written in the alternative forms

$$\begin{aligned}
 du &= T ds - p dv & \left(\frac{\partial T}{\partial v} \right)_s &= - \left(\frac{\partial p}{\partial s} \right)_v \\
 d(u - Ts) &= -s dT - p dv & \left(\frac{\partial s}{\partial v} \right)_T &= \left(\frac{\partial p}{\partial T} \right)_v \\
 d(u + pv) &= T ds + v dp & \text{hence } \left(\frac{\partial T}{\partial p} \right)_s &= \left(\frac{\partial v}{\partial s} \right)_p \\
 d(u + pv - Ts) &= -s dT + v dp & \left(\frac{\partial s}{\partial p} \right)_T &= - \left(\frac{\partial v}{\partial T} \right)_p
 \end{aligned} \tag{4.32}$$

The quantities appearing in (4.32) are called

$$\begin{aligned}
 u & \quad \text{- internal energy} \\
 f = u - Ts & \quad \text{- Helmholtz free energy, or free energy} \\
 h = u + pv & \quad \text{- enthalpy} \\
 g = u + pv - Ts & \quad \text{- Gibbs free energy, or free enthalpy.}
 \end{aligned} \tag{4.33}$$

They are also known as *thermodynamic potentials*, because their derivatives are simple variables or state functions, namely p , v , T , and s .

The equations on the right hand side of (4.32) are the integrability conditions, which follow from the alternative forms of the Gibbs equations by inspection. We shall demonstrate the usefulness of these integrability conditions by showing that the ratio of the isothermal compressibility κ_T and the adiabatic compressibility κ_s is equal to the ratio of the specific heats c_p and c_v .

The adiabatic – or isentropic – compressibility κ_s is defined as

$$\kappa_s = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_s$$

$$\begin{aligned}
&= -\frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_s \left(\frac{\partial T}{\partial p} \right)_s \quad \text{or, by (2.13): } \left(\frac{\partial v}{\partial T} \right)_s = - \left(\frac{\partial v}{\partial s} \right)_T \left(\frac{\partial s}{\partial T} \right)_v \\
&= \frac{1}{v} \left(\frac{\partial v}{\partial s} \right)_T \left(\frac{\partial s}{\partial T} \right)_v \left(\frac{\partial T}{\partial p} \right)_s \quad \text{or, by (4.32)}_2: \left(\frac{\partial v}{\partial s} \right)_T = \left(\frac{\partial T}{\partial p} \right)_v \quad \text{and with (2.13)} \\
&\quad = - \left(\frac{\partial T}{\partial v} \right)_p \left(\frac{\partial v}{\partial p} \right)_T \\
&= -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T \left(\frac{\partial s}{\partial T} \right)_v \left(\frac{\partial T}{\partial v} \right)_p \left(\frac{\partial T}{\partial p} \right)_s \quad \text{or, by: } \kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T \quad \text{and } c_v = T \left(\frac{\partial s}{\partial T} \right)_v \\
&= \frac{1}{T} \kappa_T c_v \left(\frac{\partial T}{\partial v} \right)_p \left(\frac{\partial T}{\partial p} \right)_s \quad \text{or, by (4.31)}_3 \quad \text{with } \left(\frac{\partial T}{\partial p} \right)_s = \left(\frac{\partial v}{\partial s} \right)_p \\
&= \frac{1}{T} \kappa_T c_v \left(\frac{\partial T}{\partial s} \right)_p \quad \text{or, by: } c_p = T \left(\frac{\partial s}{\partial T} \right)_p \\
&= \kappa_T \frac{c_v}{c_p}. \tag{4.34}
\end{aligned}$$

This chain of equations is typical for the calculation of relations between material coefficients. It is sometimes difficult to find the right path, because in such calculations it is easy to write down infinitely many correct equations and yet move away from the desired result.

In the above derivation we have used expressions for the specific heats c_p and c_v which were not listed before, *viz.*

$$c_v = T \left(\frac{\partial s}{\partial T} \right)_v \quad \text{and} \quad c_p = T \left(\frac{\partial s}{\partial T} \right)_p. \tag{4.35}$$

These are straightforward consequences from the previous definitions (2.20) and (2.25) when (4.32)_{1,3} are used.

Another example for the usefulness of (4.32) is the determination of the difference $c_p - c_v$ from the thermal equation of state. We have by (2.22)

$$\begin{aligned}
c_p - c_v &= \left(\frac{\partial v}{\partial T} \right)_p \left[\left(\frac{\partial u}{\partial v} \right)_T + p \right] \quad \text{or, with } \alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p \quad \text{and (4.24)} \\
&= v T \alpha \left(\frac{\partial p}{\partial T} \right)_v \quad \text{or, with } \beta = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_v \\
&= p v T \alpha \beta \quad \text{or, with } \alpha = p \kappa_T \beta \quad \text{by (2.14)} \\
c_p - c_v &= p^2 v T \kappa_T \beta^2. \tag{4.36}
\end{aligned}$$

In particular it follows that in an incompressible body the specific heats are equal.

4.2.4 Phase equilibrium. Clausius-Clapeyron equation

In Paragraph 2.4.1 we have shown that at the phase boundary between liquid and vapor we have, cf. (2.30)

$$r = h'' - h' \quad \text{or, by } h = u + p v$$

$$r = u'' + p v'' - (u' + p v'), \quad (4.37)$$

since the pressure is continuous on the boundary. r is the specific heat of evaporation. If the evaporation occurs at constant temperature T we have, by (4.18)

$$r = T(s'' - s'). \quad (4.38)$$

Note that T is also continuous at the phase boundary. Elimination of r between (4.37) and (4.38) provides

$$(u + p v - Ts)'' = (u + p v - Ts)', \quad (4.39)$$

so that *the specific Gibbs free energy is continuous at the phase boundary*, – along with T and p . We may write

$$g''(T, p) = g'(T, p), \quad (4.40)$$

and this is an implicit form of the equation $p = p(T)$ for saturated steam and boiling liquid. Unfortunately we do not know the functions $g'(T, p)$ and $g''(T, p)$ analytically, therefore we cannot have an explicit analytic form of $p(T)$.

And yet, we can make an interesting statement about $p(T)$ by writing (4.39) as

$$p(T) = - \frac{u'' - Ts'' - (u' - Ts')}{v'' - v'}, \quad (4.41)$$

where all the quantities on the right hand side are functions of T . Differentiation with respect to T provides*

$$\frac{dp}{dT} = \frac{1}{T} \frac{r}{v'' - v'}. \quad (4.42)$$

This is the *Clausius-Clapeyron equation*. We may call $p = p(T)$ and $r = r(T)$ the thermal and the caloric equations of state of saturated vapor, and then (4.42) represents a relation between these state equations, just as (4.24) implies a relation between the two equations of state of a one-phase fluid. Indeed, the Clausius-Clapeyron equation with $r = h'' - h'$ and $h = u + p v$ may be rewritten in the form

$$\frac{u'' - u'}{v'' - v'} = -p + T \frac{dp}{dT}, \quad (4.43)$$

which is clearly the analogue of the integrability condition (4.24) applied to evaporation.

* One might suspect that there must be an additional term in (4.42) due to $\frac{du''}{dT}, \frac{ds''}{dT}, \frac{dv''}{dT}$ and $\frac{du'}{dT}, \frac{ds'}{dT}, \frac{dv'}{dT}$. However, that term vanishes because of the Gibbs equation applied to the saturated vapor and the boiling liquid.

With some simplifying assumptions the Clausius-Clapeyron equation may be integrated to provide an analytic form for the saturated vapor curve $p = p(T)$. We assume

- i.) r is independent of T ,
- ii.) $v' \ll v''$,
- iii.) $v' = \frac{1}{p} \frac{R}{M} T$, i.e. vapor is considered an ideal gas,

and write (4.42) as

$$\frac{dp}{p} = \frac{r}{\frac{R}{M} T^2} dT, \text{ hence } p = p(T_0) \exp \left[-\frac{r}{\frac{R}{M}} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right], \quad (4.45)$$

where T_0 is some reference temperature. According to this equation the saturated vapor curves must be straight lines in a $(\ln p, 1/T)$ -diagram. Fig. 4.4 shows experimental curves which confirm this linearity *in the whole range of temperature between the triple point and the critical point*. This agreement is most surprising, because none of the assumptions (4.44) is very trustworthy: all are bad in the neighborhood of the critical point. We must conclude that several mistakes in the assumptions compensate each other. Anyway we are thus left with a reliable analytic form of the saturated vapor curve.

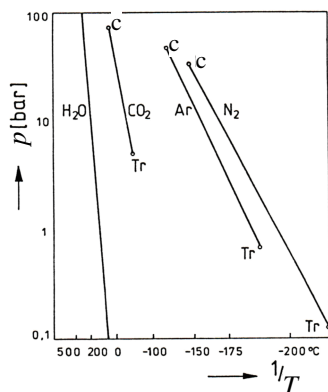
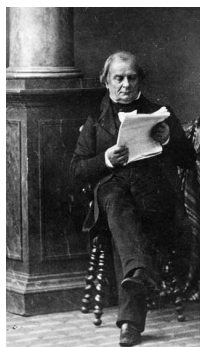


Fig. 4.4 Benoît Pierre Émile CLAPEYRON (1799-1864)

Vapor-pressure-curves in a $\left(\ln p, \frac{1}{T} \right)$ -diagram

CLAPEYRON was a professor at the École Polytechnique in Paris. He did much to clarify CARNOT's work but he could not overcome the caloric theory. Therefore he could not identify the factor $\frac{1}{T}$ in the Clausius-Clapeyron equation; this was left to do for CLAUSIUS. CLAPEYRON, however, made an everlasting contribution to p dV-thermodynamics by representing reversible processes as lines in (p, V) -diagram.

4.2.5 Phase equilibrium in a van der Waals gas

In Paragraph 2.4.9 we have discussed the isotherms of a van der Waals gas. A typical isotherm has the form shown in Fig. 4.5 a. The ascending branch, where the volume grows with increasing pressure, is physically unrealistic; later – in Paragraph 4.2.8 – we shall recognize that branch as unstable.

But even without this peculiarity the van der Waals equation provides the possibility to have two different volumes for the same pressure and the same temperature. Therefore we say that the equation can describe a fluid in the range of the phase transition liquid-vapor. The greater specific volume may then be called $v''(T)$ and the smaller one $v'(T)$.

This sounds promising. However, for a fixed temperature there is a whole range of pressures for which liquid and vapor may coexist; three such pressures are shown in Fig. 4.5 a. On the other hand we already know from the section on wet steam that there is only *one* $p(T)$, and so we must ask how we can identify this single pressure.

The answer is best given graphically by a construction which goes back to MAXWELL. We recall (4.41) and write, using $f = u - Ts$

$$p(T)(v'' - v') + f'' - f' = 0 \quad \text{or, with } f = - \int p \, dv, \text{ cf. (4.32)} \quad (4.46)$$

$$p(T)(v'' - v') - \int_{v'}^{v''} p(v, T) \, dv = 0, \quad (4.47)$$

where the integral has to be taken along the isotherm; *i.e.* the integral represents the area below the isotherm between v' and v'' . By (4.47) this area must be equal to the area of the rectangle $p(T)(v'' - v')$. Therefore we find $p(T)$ as *the* isobar – the Maxwell line – with equal areas between the isotherm above and below, cf. Fig. 4.5 b. Afterwards v' and v'' come out as shown in the figure.

It is instructive to consider this case from another point of view by use of the free energy. We have $p = -\left(\frac{\partial f}{\partial v}\right)_T$, so that the non-monotonic isotherm in the (p, v) -diagram corresponds to a non-convex isotherm in the (f, v) -diagram shown in Fig. 4.5 c. For the wet steam we write, as in Paragraph 2.4.1

$$\begin{aligned} f &= (1-x)f' + x f'' \\ v &= (1-x)v' + x v'' \end{aligned} \quad \text{or, by (4.46): } f = f' - p(T)(v - v'). \quad (4.48)$$

It follows that the free energy of the wet steam is a linear function of v with the slope $-p(T)$. Graphically this function is equal to the common tangent of the two convex parts of $f(v, T)$, cf. Fig. 4.5 c. In this manner it is obvious that the free energy of wet steam is lower than the free energy of either homogeneous phase.

The graphical methods described above are known in the literature as the “equal area rule” and as the “common tangent rule.” Mathematicians speak of the *convexification* of the free energy function.

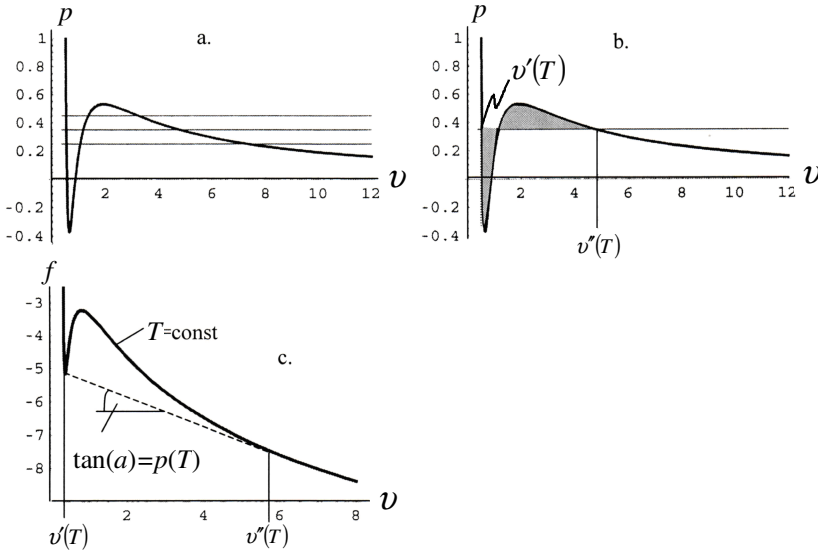


Fig. 4.5 a. Isotherm of a van der Waals gas

b. Construction of the Maxwell line $p(T)$

c. Free energy of a van der Waals gas, and of wet steam. (For a clear graphical representation the temperatures in a. and b. are different from the temperature in c.)

4.2.6 Temperature change during adiabatic throttling

Example: Van der Waals gas

Throttling is a means for decreasing the pressure of a fluid and in Paragraph 1.5.9 we have seen that during adiabatic throttling the specific enthalpy is equal in front and far behind the throttle valve. Thus we have, at least approximately

$$dh = \left(\frac{\partial h}{\partial T} \right)_p dT + \left(\frac{\partial h}{\partial p} \right)_T dp = 0 \quad \text{and therefore, with } c_p = \left(\frac{\partial h}{\partial T} \right)_p$$

$$\left(\frac{\partial T}{\partial p} \right)_h = \frac{1}{c_p} \left(\frac{\partial h}{\partial p} \right)_T. \quad (4.49)$$

This equation determines the temperature change that accompanies the pressure decrease. We proceed to replace $\left(\frac{\partial h}{\partial p} \right)_T$ by quantities that follow from the thermal equation of state. For this purpose we employ the Gibbs equation (4.19)

$$ds = \frac{1}{T} (du + p dv) \quad \text{with } p dv = d(pv) - v dp \quad \text{and } h = u + pv$$

$$ds = \frac{1}{T} (dh - v dp) \quad \text{with } h = h(T, p):$$

$$ds = \frac{1}{T} \left(\frac{\partial h}{\partial T} \right)_p dT + \frac{1}{T} \left[\left(\frac{\partial h}{\partial p} \right)_T - v \right] dp.$$

The implied integrability condition reads

$$\left(\frac{\partial}{\partial p} \left[\frac{1}{T} \left(\frac{\partial h}{\partial T} \right)_p \right] \right)_T = \left(\frac{\partial}{\partial T} \left[\frac{1}{T} \left[\left(\frac{\partial h}{\partial p} \right)_T - v \right] \right] \right)_p \Rightarrow \left(\frac{\partial h}{\partial p} \right)_T = v - T \left(\frac{\partial v}{\partial T} \right)_p. \quad (4.50)$$

Insertion into (4.49) gives

$$\left(\frac{\partial T}{\partial p} \right)_h = \frac{vT}{c_p} \left(\alpha - \frac{1}{T} \right), \text{ where } \alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p \quad (4.51)$$

is the thermal expansion coefficient, *cf.* (2.12).

For an ideal gas, where $\alpha = 1/T$ holds, there is no temperature drop during throttling. Later, *cf.* Paragraph 4.2.8, we shall show that c_p is positive and therefore (4.51) implies that in throttling we have

$$\begin{array}{ll} \text{heating} & \text{if } \alpha < \frac{1}{T} \\ \text{cooling} & \text{if } \alpha > \frac{1}{T}. \end{array} \quad (4.52)$$

As an instructive example we investigate the throttling of a van der Waals gas. The thermal equation of state is given by (2.33) so that by differentiation we have

$$dp = \frac{\frac{R}{M}}{v-b} dT - \left(\frac{\frac{R}{M} T}{(v-b)^2} - \frac{2a}{v^3} \right) dv$$

from which we determine the expansion coefficient

$$\alpha = \frac{\frac{R}{M} \frac{v-b}{v}}{\frac{R}{M} T - \frac{2a}{v} \left(\frac{v-b}{v} \right)^2}$$

and the quantity $\alpha - \frac{1}{T}$ relevant for the temperature change

$$\alpha - \frac{1}{T} = \frac{1}{vT} \frac{-b + \frac{2a}{\frac{R}{M} T} \left(\frac{v-b}{v} \right)^2}{1 - \frac{2a}{v \frac{R}{M} T} \left(\frac{v-b}{v} \right)^2}. \quad (4.53)$$

Loosely speaking the terms with a and b are small and therefore the sign of $\alpha - 1/T$ is determined by the numerator of this expression. The sign of the numerator depends on the pair (v, T) before the throttle valve (say). We have

$$\begin{array}{ll} \text{heating} & \text{for } \frac{v-b}{v} > \sqrt{\frac{\frac{R}{M} T}{2 \frac{a}{b}}} \text{ or } v > \frac{1}{3 - 2\sqrt{\frac{1}{3}\gamma}} \\ \text{cooling} & \text{for } \frac{v-b}{v} < \sqrt{\frac{\frac{R}{M} T}{2 \frac{a}{b}}} \text{ or } v < \frac{1}{3 - 2\sqrt{\frac{1}{3}\gamma}} \end{array} \quad (4.54)$$

In (4.54)₂ we have used dimensionless variables in order to emphasize the universal properties of the van der Waals equation, *cf.* (2.34), (2.35). We conclude that the curve

$$v = \frac{1}{3 - 2\sqrt{\frac{1}{3}\gamma}}, \text{ or } \gamma = \frac{3}{4} \left(3 - \frac{1}{v} \right)^2. \quad (4.55)$$

divides the first quadrant of the (v, γ) -space into two regions: one where cooling occurs and one for heating. This curve is called the inversion curve; it may also be calculated in a (π, γ) - or a (π, v) -diagram by use of the van der Waals equation of state (2.36). We obtain

$$\pi = 24\sqrt{3}\sqrt{\gamma} - 12\gamma - 27 \quad \text{or} \quad \pi = \frac{18}{v} - \frac{9}{v^2}. \quad (4.56)$$

Fig. 4.6 shows these graphs and also – as a thin line – the critical isochor and the critical isotherm, respectively. The regions of heating and cooling are indicated.

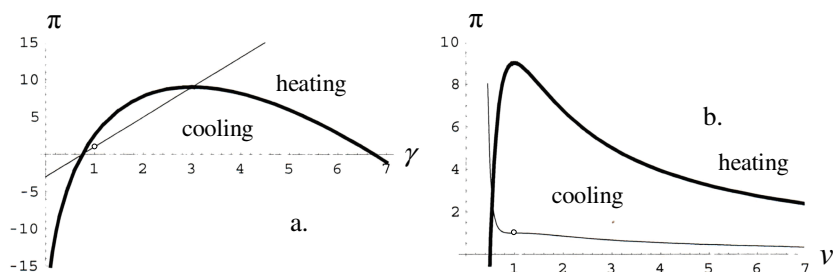


Fig. 4.6 a. Inversion curve and critical isochor $\pi = 4\gamma - 3$

b. Inversion curve and critical isotherm $\pi = \frac{8}{3v-1} - \frac{3}{v^2}.$

For nitrogen, oxygen, and hydrogen we have listed critical data in Table 4.1. It follows from this data that those gases have the following dimensionless pressures and temperatures at 1 bar and 300 K

$$\begin{array}{lll} \pi_{\text{N}_2} = 0.03 & \pi_{\text{O}_2} = 0.02 & \pi_{\text{H}_2} = 0.08 \\ \gamma_{\text{N}_2} = 2.4 & \gamma_{\text{O}_2} = 1.9 & \gamma_{\text{H}_2} = 9.1. \end{array}$$

For hydrogen these data place the state (1 bar, 300 K) firmly outside the region of cooling, so that hydrogen heats up by throttling from this state.

Therefore hydrogen-carrying pipes must be carefully sealed, because escaping – throttled – hydrogen forms a highly explosive mixture with air and can easily be ignited at the leak where the gas heats up. Most other gases are cooled at a leak, – so also O_2 and N_2 .

JOULE and THOMSON (LORD KELVIN) have first observed the cooling of gases by throttling. From the molecular point of view the phenomenon is easy to understand. By reducing the pressure we increase the specific volume and therefore the mean distance of the molecules. According to Fig. 2.12 a this means that the potential energy of the molecular interaction grows, and – since the process is adiabatic – the kinetic energy, hence the temperature must drop. The temperature drop is bigger, if the gas was colder before the throttle valve.

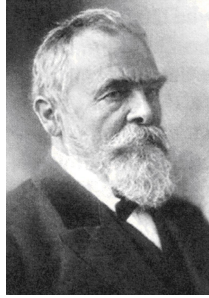
Table 4.1 Critical values of N₂, O₂, and H₂

	p_c [bar]	T_c [K]
N ₂	34.5	126
O ₂	51.8	155
H ₂	13.2	33

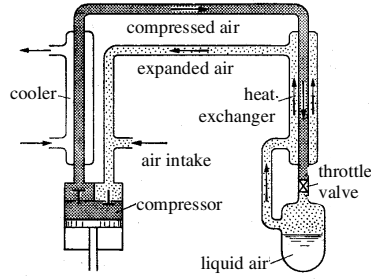
Louis Paul CAILLETET (1832-1913) used this observation to liquefy small amounts of oxygen by throttling and Carl Ritter VON LINDE (1842-1934) invented a clever repetitive process in order to liquefy large amounts of air for technical purposes. He used the throttled air for pre-cooling newly supplied air before throttling it, and then he used that throttled air for pre-cooling yet more air, *etc.* LINDE succeeded to construct a continuous process upon this principle. Thus liquid air became a commodity when before it had been a scientific curiosity.



Louis Paul Cailletet



Carl Ritter von Linde



Linde's liquefying apparatus

4.2.7 Available free energies

We have seen that the entropy in an adiabatic system cannot decrease, so that in equilibrium – when all rates of change have come to an end – the entropy assumes its maximal value. We write

$$S \Rightarrow \text{maximum in an adiabatic body.} \quad (4.57)$$

This is the prototype of all thermodynamic stability conditions. There are alternatives for non-adiabatic bodies, and we proceed to derive those.

We rely on the first and second laws for this purpose and write, – *cf.* Paragraphs 1.5.2 through 1.5.5 and 4.1.2 – ignoring radiation

$$\frac{d(U + E_{\text{pot}} + K)}{dt} = \dot{Q} + \dot{W}_{\text{stress}}, \quad \text{where} \quad \dot{W}_{\text{stress}} = \int_{\partial V} t_{ij} w_i n_j dA$$

$$\frac{dS}{dt} \geq \frac{\dot{Q}}{T}, \quad (4.58)$$

where T is a homogeneous temperature on ∂V . Elimination of \dot{Q} provides

$$\frac{d(U + E_{\text{pot}} + K - TS)}{dt} \leq -S \frac{dT}{dt} + \int_{\partial V} t_{ij} w_i n_j dA . \quad (4.59)$$

If the surface temperature is constant – as well as homogeneous – and if the surface does not move, so that its velocity is zero, we have the stability condition

$$U + E_{\text{pot}} + K - TS \Rightarrow \text{minimum for } T=\text{const and } w_i = 0 \text{ on } \partial V . \quad (4.60)$$

Note that inside V anything and everything may occur initially: turbulent motion, friction, heat conduction, phase changes, chemical reactions, *etc.* As long as the surface is at rest and has a constant homogeneous temperature, the expression $U + E_{\text{pot}} + K - TS$ tends to a minimum as equilibrium is approached. Consequently we conclude that a *decrease of energy* is conducive to equilibrium and so is an *increase of entropy*. In a manner of speaking we might say that the energy *wants* to reach a minimum, and that the entropy *wants* to reach a maximum.

There is another interpretation of (4.59) when ∂V contains a movable part on which $t_{ij} = -p\delta_{ij}$ holds with a homogeneous pressure p , prescribed and maintained

there. In that case $\int_{\partial V} t_{ij} w_i n_j dA = -p \frac{dV}{dt}$ holds and we may write

$$\frac{d(U + E_{\text{pot}} + K - TS)}{dt} \leq -S \frac{dT}{dt} - p \frac{dV}{dt} .$$

So, if the surface temperature is constant and homogeneous on ∂V , and if p is constant and homogeneous on its movable part, we have the stability condition

$$U + E_{\text{pot}} + K + pV - TS \Rightarrow \text{minimum, for } T=\text{const on } \partial V \text{ and for } p=\text{const on its movable part.} \quad (4.61)$$

These arguments illustrate that the thermodynamic stability conditions – just as mechanical ones – depend on the system and on its thermo-mechanical loading. The foregoing considerations do not in any way exhaust the possibilities: Indeed, the quantity that must be minimized, or maximized, may be different for different problems and must be carefully identified by the exploitation of the two relations (4.58) in each case. Generically we may call that quantity the *available free energy* and we shall usually denote it by the letter \mathcal{A} .

The above considerations indicate that, if the surface temperature T is small, \mathcal{A} tends to a minimum, because its energetic part does. If, on the other hand, T is large, \mathcal{A} tends to a minimum, because the entropy tends to a maximum. In general, however, – for intermediate values of T – both tendencies, the energetic one and the entropic one, have to compromise. We shall later treat some illustrative examples of this competition.

Note that the T in (4.58) through (4.61) is the homogeneous temperature of the surface ∂V and that p in (4.61) is the homogeneous pressure on the movable part of ∂V . Therefore the available free energies in (4.60) and (4.61) are not the Helmholtz free energy and Gibbs free energy, – not even without the kinetic energy K . How could they? After all, there is generally no single T , nor a single p inside V . Having said this, we must qualify: It is often the case that in the approach to equilibrium the temperature and the pressure are first to assume homogeneous

values inside V , and the kinetic energy K becomes homogeneously zero, while other processes – like phase transitions and chemical reactions – are still approaching equilibrium. In such cases the availabilities $U + E_{\text{pot}} + K - TS$ in (4.60) and $U + E_{\text{pot}} + pV - TS$ in (4.61) are indeed the Helmholtz and Gibbs free energies, respectively, – plus the potential energy –, and they approach a minimum after the velocity and the gradients of temperature and pressure are “relaxed” to zero.

4.2.8 Stability conditions

We consider the situation, where in an adiabatic container of volume V a fixed piston divides a fluid into equal masses m with the states U_1, V_1 and U_2, V_2 . The entropy of both parts together is the sum of the entropies of the individual parts

$$S_{\text{tot}}(U_1, V_1, U_2, V_2) = S(U_1, V_1) + S(U_2, V_2) \quad (4.62)$$

S_{tot} depends on four variables, but only two of them are independent, since we have $V = V_1 + V_2$ and $U = U_1 + U_2$ and both are constant. Let (U_1, V_1) be the independent pair.

If the piston is now allowed to move, the entropy S_{tot} tends to a maximum – by (4.57) – and we obtain as sufficient condition for the eventual equilibrium

$$\frac{\partial S_{\text{tot}}}{\partial U_1} = 0, \quad \frac{\partial S_{\text{tot}}}{\partial V_1} = 0, \quad \frac{\partial^2 S_{\text{tot}}}{\partial U_1 \partial U_1} \delta U_1^2 + 2 \frac{\partial^2 S_{\text{tot}}}{\partial U_1 \partial V_1} \delta U_1 \delta V_1 + \frac{\partial^2 S_{\text{tot}}}{\partial V_1 \partial V_1} \delta V_1^2 < 0 \quad (4.63)$$

for arbitrary small values of $\delta U_1, \delta V_1$. By use of (4.62) we obtain

$$\left(\frac{\partial S}{\partial U_1} \right)_{V_1} = \left(\frac{\partial S}{\partial U_2} \right)_{V_2}, \quad \text{and} \quad \left(\frac{\partial S}{\partial V_1} \right)_{U_1} = \left(\frac{\partial S}{\partial V_2} \right)_{U_2} \quad \text{and} \quad (4.64)$$

$$\frac{\partial^2 S}{\partial U_1^2} \delta U_1^2 + 2 \frac{\partial^2 S}{\partial U_1 \partial V_1} \delta U_1 \delta V_1 + \frac{\partial^2 S}{\partial V_1^2} \delta V_1^2 < 0. \quad (4.65)$$

By the Gibbs equation (4.19) the equations (4.64) imply $T_1 = T_2$ and $p_1 = p_2$ – not unexpectedly for an equilibrium condition. The inequality (4.65) indicates that the entropy is a concave function of U_1 and V_1 . For simplicity we drop the index 1 and write (4.65) in the form

$$\left[\frac{\partial}{\partial U} \left(\frac{\partial S}{\partial U} \right) \delta U + \frac{\partial}{\partial V} \left(\frac{\partial S}{\partial U} \right) \delta V \right] \delta U + \left[\frac{\partial}{\partial U} \left(\frac{\partial S}{\partial V} \right) \delta U + \frac{\partial}{\partial V} \left(\frac{\partial S}{\partial V} \right) \delta V \right] \delta V < 0.$$

By $\frac{\partial S}{\partial U} = \frac{1}{T}$ and $\frac{\partial S}{\partial V} = \frac{p}{T}$ we obtain

$$\delta \left(\frac{1}{T} \right) \delta U + \delta \left(\frac{p}{T} \right) \delta V < 0.$$

We insert

$$\delta U = \left(\frac{\partial U}{\partial T} \right)_V \delta T + \left(\frac{\partial U}{\partial V} \right)_T \delta V = mc_v \delta T + \left(-p + T \left(\frac{\partial p}{\partial T} \right)_V \right) \delta V \quad \text{and}$$

$$\delta\left(\frac{p}{T}\right) = -\frac{p}{T^2}\delta T + \frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_V \delta T + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T \delta V$$

so that a quadratic form follows without a mixed term, *viz.*

$$-\frac{1}{T^2}c_v(\delta T)^2 + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T (\delta V)^2 < 0. \quad (4.66)$$

Since this must hold for arbitrary small values of δT and δV , the inequality implies, *cf.* (2.12)

$$c_v > 0 \quad \text{and} \quad \kappa_T > 0. \quad (4.67)$$

The specific heat c_v and the compressibility κ_T are positive.

We conclude that isochoric heating will always raise the temperature and that an isothermal increase of pressure will always decrease the volume. Both phenomena correspond so clearly to everyday experience, that any other result would be absurd. However, it is interesting to note that our experience conforms to the second law, since the present result is a direct consequence of that law.

The inequalities (4.67) have corollaries that are not quite as obvious. Indeed, by (4.34) and (4.36), they imply

$$\kappa_T > \kappa_S \quad \text{and} \quad c_p > c_v. \quad (4.68)$$

These relations are therefore also consequences of the Second Law. Nor are they the only corollaries of (4.67). A particularly interesting one results from (4.36) (2.14) and (4.68). It concerns the thermal expansion coefficient α^2 and it reads

$$\alpha^2 < \frac{1}{vT}c_p\kappa_T. \quad (4.69)$$

It follows that a vanishing compressibility implies that there is no thermal expansion either, *i.e.* the density ρ is strictly constant in an incompressible body; it depends neither on p nor T .

The conditions (4.67) through (4.69) are called thermodynamic stability conditions. They are universal restrictions on constitutive properties. If there existed a material, in which the restrictions did not apply, the Second Law would be violated by processes in such materials.

4.2.9 Specific heat cp is singular at the critical point

It is clear from (4.67)₂ that the van der Waals isotherms for $T < T_C$ violate thermodynamic stability in a range of states where $\frac{\partial p}{\partial v} > 0$ holds. Such states are unwanted byproducts of the statistical mechanical derivation of the van der Waals equation, and under most circumstances they must be ignored.* This is effectively done by the convexification procedure described in Paragraph 4.2.5.

The lowest monotonically decreasing isotherm is the critical one which, however, also violates thermodynamic stability, albeit in a single point, namely the critical point, where $\frac{\partial p}{\partial v} = 0$ holds. The caloric equation of state also exhibits a singular behavior in that point. In order to see that we consider the specific heats.

* The unstable states play a certain role in the investigation of hysteretic phenomena, *cf.* Sect. 12.5.

We have already seen, *cf.* (4.27) that c_v in a van der Waals gas depends on T only and for the present purposes we take it to be constant.* On the other hand c_p is given by (4.36) as

$$c_p - c_v = vT\kappa_T \left(\frac{\partial p}{\partial T} \right)_v^2.$$

κ_T is infinite at the critical point, while $\frac{\partial p}{\partial T}$ is finite. Therefore, as we approach the critical point, c_p tends to infinity. Fig. 4.7 shows graphs of c_p for superheated water vapor which illustrate the emerging singularity as the critical point is approached.

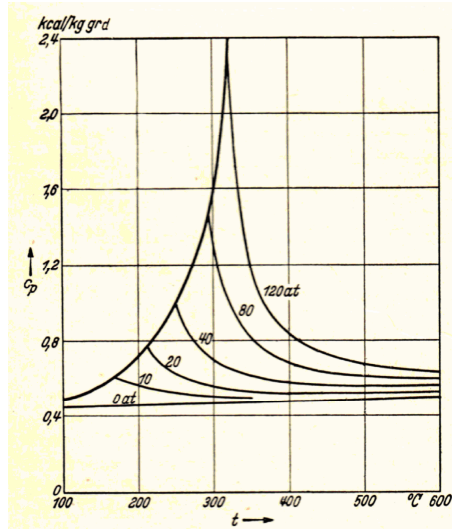


Fig. 4.7 c_p for superheated water vapor as a function of temperature.

Points on the concave limiting curve correspond to saturated vapor.

[The graph is taken from E.Schmidt, *Thermodynamik*. Springer, published in 1956. Hence the archaic units]

4.3 A layer of liquid heated from below – onset of convection

We consider a horizontal fluid layer of thickness D . The fluid is at rest and in a stationary state with respect to the density ρ and temperature T ; it is heated from below so that the temperatures on top and at the bottom are T_D and T_0 , respectively, with $T_0 > T_D$. The mass balance is identically satisfied and the balance of momentum and energy read

$$\text{momentum balance } \frac{dp}{dx} = -\rho g \quad \text{with } p=p(\rho, T)$$

* The reference to the van der Waals equation is only convenient, not essential; the result of this paragraph holds for all fluids.

energy balance $\frac{dq}{dx} = 0$ with $q = -\kappa \frac{dT}{dx}$.

Hence follows for a constant thermal conductivity κ

$$T(x) = T_0 + \frac{T_D - T_0}{D} x, \text{ and}$$

$$\underbrace{\left(\frac{\partial p}{\partial \rho}\right)_T}_{\frac{1}{\rho \kappa_T}} \frac{d\rho}{dx} + \underbrace{\left(\frac{\partial p}{\partial T}\right)_\rho}_{\frac{\alpha}{\kappa_T}} + \frac{T_D - T_0}{D} = -\rho g, \quad (4.70)$$

where the isothermal compressibility κ_T and the thermal expansion coefficient α may be introduced to give

$$\left. \frac{d\rho}{dx} \right|_{\text{rest}} = \alpha \rho \frac{T_0 - T_D}{D} - \rho^2 \kappa_T g. \quad (4.71)$$

This is the density gradient in the layer at rest. We conclude that the gradient is bigger than in an isothermal layer,* although generally still negative.** Thus for a given temperature T_D the fluid is lighter at the bottom than in the isothermal case. This may be suspected to be an unstable situation.

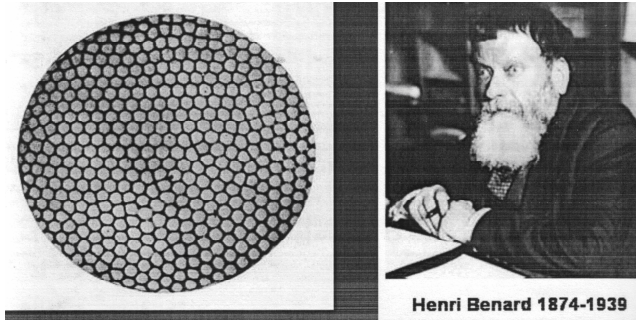


Fig. 4.8 Hexagonal convection cells. Henri Bénard, a pioneer of convection processes

Namely, the relatively light fluid at the bottom – relative to the isothermal case – may have a tendency to rise; or else, the relatively heavy fluid at the top has a tendency to sink. Observations show that this is indeed the case: The rising and sinking occurs in “convection bubbles” such that a light “bubble” rises and pushes the heavier fluid at the top sideways; subsequently that heavier fluid is sucked down into the space that opens below it when the ascending fluid is replaced by a horizontal flow at the bottom. In this way – after some time – a stationary pattern appears with fluid moving upwards, sideways and downwards. If the boundaries

* As long as $\alpha > 0$ is assumed which is usually the case, barring the anomaly of water between 0°C and 4°C .

** Of course, if T_0 is sufficiently bigger than T_D , the density may actually grow with height.

of the fluid permit it, the pattern is geometrically regular, and it may consist of hexagonal *convection cells* as shown in Fig. 4.8.

The rising and sinking bubbles are essentially adiabatic, because the thermal conductivity is too small to allow for an effective exchange of heat between the bubbles and the surrounding fluid. We use the adiabaticity to calculate the density gradient in the center of a cell, where the fluid moves vertically upwards. This gradient is called the *adiabatic density gradient*. We have

$$\begin{aligned}
 \dot{q}dt &= du + p dv = 0 \quad \text{or} \\
 dh - v dp &= 0 \\
 \underbrace{\left(\frac{\partial h}{\partial T}\right)_p}_{c_p} \frac{dT}{dx} + \underbrace{\left(\left(\frac{\partial h}{\partial p}\right)_T - v\right)}_{-T\left(\frac{\partial v}{\partial T}\right)_p} \frac{dp}{dx} &= 0 \\
 c_p \left(\frac{\partial T}{\partial \rho}\right)_p \frac{d\rho}{dx} + \left(c_p \left(\frac{\partial T}{\partial p}\right)_p - T \left(\frac{\partial v}{\partial T}\right)_p\right) \underbrace{\frac{dp}{dx}}_{-\rho g} &= 0 \\
 c_p \frac{d\rho}{dx} + \left(c_p \left(\frac{\partial \rho}{\partial p}\right)_T - \frac{T}{\rho^2} \left(\frac{\partial \rho}{\partial T}\right)^2\right) \rho g &= 0
 \end{aligned}$$

Therefore we obtain

$$\left. \frac{d\rho}{dx} \right|_{\text{convection}} = \frac{g\alpha^2 \rho T}{c_p} - \rho^2 \kappa_T g. \quad (4.72)$$

Thus both gradients, the one for the fluid at rest and the convective – adiabatic – one, are bigger than the isothermal gradients, so that both situations are possibly unstable. It is now a question which of the situations is “more unstable” and concerning this we assume that the fluid at rest is stable, if

$$\left. \frac{d\rho}{dx} \right|_{\text{rest}} \leq \left. \frac{d\rho}{dx} \right|_{\text{convection}}. \quad (4.73)$$

Otherwise the stationary convection is stable. The idea is this: When a bubble starts to rise and its density becomes larger than the density of the surrounding fluid at rest, the bubble will sink back and stability of the rest state is maintained. By (4.71), (4.72) the criterion (4.73) places a condition on the maximal value of $T_0 - T_D$ for which the fluid can be at rest, namely

$$\frac{T_0 - T_D}{D} \leq \frac{g\alpha T}{c_p} \quad (\text{stability of the state of rest}). \quad (4.74)$$

By (4.72) – after an easy calculation – we see that the condition (4.74) is tantamount to saying that, for convection to occur, the temperature gradient of the rest-solution exceeds the adiabatic temperature gradient.

If the criterion (4.73) is believed, this inequality provides a necessary condition for stability of the rest state. We have ignored viscosity in the argument which,

however, may serve to keep the fluid at rest up to a bigger temperature gradient T_0-T_D than the one implied by (4.74). Viscosity, *i.e.* internal friction, may delay the onset of motion.*

So far, entropy was not mentioned in the argument. However, if we introduce entropy, we obtain yet another suggestive form of the stability criterion for the state of rest. Since the fluid in the rising bubble undergoes a reversible adiabatic change, we have $\left.\frac{ds}{dx}\right|_{\text{convection}} = 0$. On the other hand, the entropy gradient for the fluid at rest reads

$$\begin{aligned}\left.\frac{ds}{dx}\right|_{\text{rest}} &= \underbrace{\left(\frac{\partial s}{\partial p}\right)_T}_{-\alpha v} \underbrace{\frac{dp}{dx}}_{\rho g} + \underbrace{\left(\frac{\partial s}{\partial T}\right)_p}_{\frac{1}{T}c_p} \underbrace{\frac{dT}{dx}}_{\frac{T_D-T_0}{D}} \\ \left.\frac{ds}{dx}\right|_{\text{rest}} &= \frac{c_p}{T} \left(\frac{T_D-T_0}{D} + \frac{\alpha g T}{c_p} \right).\end{aligned}\quad (4.75)$$

Comparison with (4.74) shows that the rest state is stable as long as $\left.\frac{ds}{dx}\right|_{\text{rest}} \geq 0$, *i.e.* as long as the entropy grows with height.

Convection plays an important role in the heating of our houses. Indeed, the warm air on top of the heater, – sometimes called “radiator” – rises and pushes the cold air near the ceiling down into contact with the heater. Thus a convection cell develops in our rooms and that is responsible for efficient, more or less homogeneous heating. If the heating of a room had to rely on conduction, it would take a very long time indeed.

On a larger scale convection of air, and thermal updrafts, are responsible for the mixing of air in the lower atmosphere. If the air contains moisture, the upward convection – and the concomitant adiabatic cooling – creates cumulus clouds, the “good weather clouds” on a fine summer day. We describe that phenomenon in Paragraph 10.4.

On the global scale convection creates the earth-spanning convection cells: The Hadley cells on both sides of the equator, the Ferrell cells in the temperate zones of the earth, and the polar cells. To a very large extent these convection cells are responsible for the moderate temperatures on much of the earth’s surface.

We have already discussed the convection in water and the seas, *cf.* Paragraph 2.4.4. In that case the anomaly of water – with $\alpha < 0$ – adds a complication according to (4.71). But the complication is benign; it helps to make the earth habitable as we have argued in Chapter 2.

Finally convection plays a very important part in stars like the sun, because it is essential for the transport of the nuclear heat in the inner core of the star to the surface.

For all this confirmed importance of convection we must realize that the stability criterion (4.74) is *ad hoc*. It may be plausible but it does not follow from the Second Law – or not in any way that we are aware of.

* A proper mathematical treatment of this problem does not use the condition (4.73). It proceeds by a linear stability analysis of the field equations, – including viscous terms –, under small disturbances. That treatment requires numerical methods and it is outside the scope of this book.

4.4 On the history of the Second Law

Apart from Clausius, whose ideas we have discussed in detail, we must mention Nicolas Léonard Sadi CARNOT (1796-1832) as one of the forerunners of the Second Law. CARNOT's work *Reflexions sur la Puissance Motrice du Feu et sur les Machines Propres a développer cette Puissance* appeared in 1824. At that time there were already thousands of steam engines at work – most of them in England – and their efficiency was less than 10%.

CARNOT posed the question, whether and how the efficiency might be increased. Everything seemed possible: It seemed conceivable that the efficiency could be improved by changing the process of the steam engines, or by replacing water as the working agent by some other material, e.g. mercury or sulphur. CARNOT obtained two results in this matter.

- The maximal efficiency of a heat engine working between a highest temperature T_H and a lowest temperature T_L occurs when the engine exchanges heat only at those temperatures. That process is now called a Carnot process, and CARNOT writes that it is
... le plus avantageux possible, car il ne s'est fait aucun rétablissement inutile d'équilibre dans le calorique.
- The efficiency of a Carnot engine is a universal function of T_H and T_L . It is independent of the working agent and does not depend either on the volume or pressure range that is covered by the process. In CARNOT's words:

Le maximum de puissance motrice résultant de l'emploi de la vapeur est aussi le maximum de puissance motrice réalisable par quelque moyen que ce soit.

In the shortest possible form this means that

The Carnot efficiency is maximal and universal.*

That CARNOT could arrive at these correct conclusions, shows the power of his intuition rather than his physical insight. Indeed, CARNOT's argument is largely based on the then prevalent caloric theory, by which heat was considered a weightless fluid.

The caloric theory assumed that the caloric – the heat stuff – is added to an engine in the boiler and comes out of the cooler, *unchanged in amount*. In the transition from boiler to cooler heat was supposed to perform work much as water does when it falls from a height. That is a plausible idea, perhaps, but it turned out to be wrong.

It was left to CLAUSIUS to correct these ideas. He did this in 1854 in his work: *Über eine veränderte Form des zweiten Hauptsatzes der mechanischen Wärmetheorie*. In that work he calculates the efficiency of a Carnot engine and he confirms CARNOT's statements about the efficiency. CLAUSIUS comes to the conclusion that it is Q/T – not Q itself – that passes through a heat engine from boiler to cooler unchanged in amount and that quantity he calls the *entropy*. The motivation for inventing this word is a little vague: CLAUSIUS envisages changes of heat to work and of heat of high temperature to heat of low temperature, and he sees entropy as a measure for the capacity of such changes. He says:

Ich habe den Vorschlag gemacht, diese Verwandlung nach dem griechischen Wort τροπή die Entropie des Körpers zu nennen.

* CARNOT did not have the form $1 - \frac{T_L}{T_H}$ for the efficiency. That came 30 years later with

CLAUSIUS in 1854.



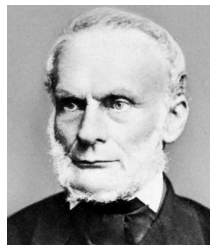
... on peut comparer avec assez de justesse la puissance motrice de la chaleur à celle d'une chute d'eau : toutes deux ont une maximum que l'on ne peut pas dépasser, quelle que soit d'une part la machine employée à recevoir l'action de l'eau, et quelle que soit de l'autre la substance employées à recevoir l'action de la chaleur. La puissance motrice d'une chute d'eau dépend de sa hauteur et de la quantité du liquide ; la puissance motrice de la chaleur dépend aussi de la quantité de calorique employé, et de ce ... que nous appellerons en effet la hauteur de sa chute, c'est à dire de la différence de température.

From the beginning the entropy met with great interest in Western science and it provoked opposition. The criticism was directed primarily against the teleological tendency expressed by the entropy *inequality*, e.g. (4.22). The monotonic trend to a featureless homogeneous equilibrium ran counter to the idealistic idea of progress to an ever more complex world. And it was not only natural scientists who concerned themselves with entropy, but also philosophers, sociologists, and historians.

CLAUSIUS himself had provided the catchword: He pointed out that the entropy of the universe – presumably an adiabatic system – could only grow until, in a final equilibrium, the universe would die the *heat death*.

It is often said – remarks CLAUSIUS – that the world runs in a cycle. The second law of the mechanical theory of heat contradicts that idea most decisively. Indeed, one must conclude that in all natural phenomena the total value of entropy can never decrease. The entropy tends to a maximum.

The closer the world approaches that limiting value – the maximum of entropy – the fainter will be the causes for a further change and eventually, when the maximum is reached, no change can occur anymore. The world is then in a dead stagnant state.

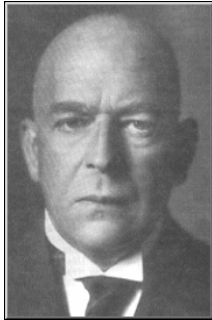
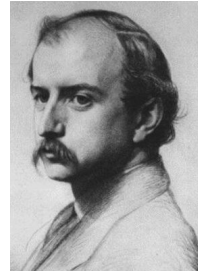


Johann Joseph LOSCHMIDT (1821-1895) deplored the *terroristic nimbus* of the second law which lets it appear as a destructive principle of all life in the universe.

The American historian Henry ADAMS (1838-1918) cites CLAUSIUS's formulation of the second law and has this to say:

For the ordinary and unsophisticated historian this only means that the ash heap grows ever bigger.

It should be noted that ADAMS was an inveterate pessimist; he considered optimism as a sure sign of idiocy.



Ostwald SPENGLER (1880-1936) an illustrious historian and philosopher – author of the book *The Decline of the West* – philosophized on entropy as follows:

The end of the world as the completion of an intrinsically necessary development – that is the twilight of the gods [of Germanic mythology]; therefore the doctrine of entropy is the last, non-religious version of the myth.

With such extrapolations of thermodynamics it is not always entirely clear what the authors think when they speculate about the First and Second Law. Let us therefore also quote a knowledgeable American jester who succinctly formulated the laws with respect to heat and work and efficiency thus:

1st Law: *You can't win.*

2nd Law: *You cannot even break even.*